

# (12) UK Patent Application (19) GB (11) 2 147 287 A

(43) Application published 9 May 1985

(21) Application No 8423318

(22) Date of filing 14 Sep 1984

(30) Priority data

(31) 837508

(32) 30 Sep 1983

(33) US

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(51) INT CL<sup>4</sup>  
C04B 35/10

(52) Domestic classification  
C1J 14 19 S X

(56) Documents cited  
None

(58) Field of search  
C1J

## (54) Alkali-resistant refractory compositions

(57) A refractory composition particularly useful in constructing glass furnaces is based primarily on silica (16-20%), alumina (67-75%), and zirconia (14-20%), wherein the silica content is primarily tied up in zircon. As a result of the silica content being bound in zirconia, less silica is available to form aluminosilicates which have a tendency to react with sodium vapors to form sodium aluminosilicates, which, during furnace operation, causes the refractory to spall or flake off. The composition can be formed using inorganic bubbles having reduced weight and, accordingly, is particularly advantageous in forehearth superstructures of glass furnaces.

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## SPECIFICATION

## Alkali-resistant refractory compositions

- 5 The present invention relates to the manufacture of refractories which are resistant to attack by sodium vapors. More particularly, the invention is directed to the manufacture of refractories useful in glass furnaces and, because of the ability to form the refractories in a form having reduced weight, highly advantageous in forehearth and superstructures of glass furnaces. 5
- Refractories useful in glass furnaces which are highly resistant to thermal shock and to corrosion by molten glass have been described in U.S. Patent No. 3,437,499, issued April 8, 1969, and assigned to the assignee of the present invention. The '499 patent describes the use of a mixture composed of zircon, 10 stabilized zirconia, alumina, mullite, clay, and calcined kyanite in water. The mixture is molded and then sintered at a temperature below the decomposition temperature of zircon. It has been found that the aforesaid refractory compositions are not completely satisfactory as refractories in certain furnaces due to 15 their tendency to spall because of the mullite component. In such glass furnaces (for example, those where alkali vapors are formed) the mullite is unstable in the presence of alkali vapors. Moreover, conventional mullite refractories are also unsatisfactory in such furnaces.
- The distress of conventional mullite refractories used in a glass furnace was determined to be the result of (1) rapid temperature change, and (2) mineralogical alteration of the mullite structure due to the presence of 20 alkalis at elevated temperatures. Alkali vapors cause decomposition of the mullite, resulting in the formation of compounds which, because of accompanying volume changes, are detrimental to service life, primarily as a result of spalling or flaking off of the refractory. The volume change has been found to be as high as 4.5% under optimum conditions. The volume change has been found to take place at approximately 2200 to 2300°F. or lower, depending upon ambient conditions within the range of temperature changes that 25 normally occur in container glass furnaces. The rate of reaction may vary depending upon the physical characteristics of the refractory, i.e., density, porosity, pore structure, and the like.
- A primary object of the present invention is to provide a refractory which can be produced by conventional methods and can be used in high alkali vapor conditions such as those found in industrial operations utilizing and/or producing slags and glasses containing compounds of sodium, potassium, calcium, 30 magnesium, and boron.
- Another object of the present invention is to provide complex refractory shapes such as those useful in glass furnace forehearth and/or superstructures having reduced weight.
- These and other objects of the present invention will be more apparent from the following disclosure and working embodiment. According to the present invention, a refractory is provided comprising as essential 35 components silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and zirconia ( $\text{ZrO}_2$ ) with traces of other components such as titania ( $\text{TiO}_2$ ) and iron ( $\text{Fe}_2\text{O}_3$ ). Compositions formulated in accordance with the present invention provide refractories which have good resistance to attack by alkali vapors, such as sodium and potassium vapors, normally associated with the manufacture of glass in a glass furnace. It is theorized that the high resistance to alkali vapors at the conditions of industrial operations utilizing and/or producing slags and glasses is a 40 result of having substantially all of the silica present in the formulation tied up or bound in the zircon which limits the availability of silica available to form sodium aluminosilicates, which, it has been found, at temperatures of certain furnace operations, are accompanied by large volume changes. By reducing the reaction of silica to form the sodium aluminosilicates it was possible to reduce the tendency of the reaction layer of the refractory to spall or flake off especially when the furnace of a part thereof, such as a glass 45 furnace forehearth, is cooled down and then heated to operating temperatures.
- Accordingly, the present invention eliminates mullite as the major component and eliminates other components (such as free silica) from the formulation in percentages which will form aluminosilicates, thereby preventing the reaction of the refractory with alkali vapors and, thus, eliminating the slabbing off or spalling problem associated with the reaction of mullite-type refractories with alkali vapors. The 50 alumina-zirconia-silica bond of the refractories of the present invention will reach equilibrium and/or stabilization during furnace operation, retarding further reaction of the alkalis with the refractory due to the absence of extensive aluminosilicates found in mullite-type or mullite-bonded refractories.

The chemical composition and analysis of the alumina-zirconia-silica refractories of the present invention are as follows:

	<i>Materials</i>	<i>Operable Range</i>	
5	Bell Clay or Kaolin	0 - 6%	5
	Ultrax 2 microns Wet Milled (Zircon)		
	Zircopax A 2 microns Wet Milled (Zircon)	15 - 25%	
	Calcined Alumina - 325 Mesh	20 - 30%	
10	Calcined Kyanite - 35 Mesh	0 - 23%	10
	Tabular Alumina - 14 Mesh	0 - 25%	
	Fused Alumina Bubbles - 4 Mesh & Finer	30 - 40%	
	<i>Chemical Analysis</i>	<i>Operable Range</i>	
15	Silica (SiO <sub>2</sub> )	10 - 16%	15
	Alumina (Al <sub>2</sub> O <sub>3</sub> )	67 - 75%	
	Zirconia (ZrO <sub>2</sub> )	14 - 20%	
	Other Oxides	1 - 2%	

20 The compositions of the present invention can be formed into refractories utilizing conventional techniques. The compositions can be employed as dense powders, flakes, or they can be formed using inorganic refractory bubbles. Utilization of bubbles permits the formation of lightweight refractory structures having particular application in lightweight super-structures for container glass forehearth. Alternatively, 25 however, the structures can be utilized with advantage in any refractory where alkali vapors are likely to be present.

#### *Example*

A refractory having the composition -

30	<i>Materials</i>		30
	Bell Clay or Kaolin	4.0%	
	Ultrax 2 microns Wet Milled (Zircon)	6.5%	
35	Zircopax A 2 microns Wet Milled (Zircon)	13.3%	35
	Calcined Alumina - 325 Mesh	21.5%	
	Calcined Kyanite - 35 Mesh	22.7%	
	Tabular Alumina - 14 Mesh	0%	
40	Fused Alumina Bubbles - 4 Mesh & Finer	32.0%	40
	<i>Chemical Analysis</i>		
	Silica (SiO <sub>2</sub> )	15.9%	
	Alumina (Al <sub>2</sub> O <sub>3</sub> )	68.3%	
45	Zirconia (ZrO <sub>2</sub> )	15.7%	45
	Other Oxides	0.6%	

was placed in a paddle mixer and blended at a low mixer speed. A polyelectrolyte and water was added to the dry mix, and mixing continued to form a semi-fluid mass. The semi-fluid mass, after thorough mixing, 50 was placed in a plaster mold and air dried after removal from the mold. The molded refractory was then heated at about 220°F. to remove remaining water and thereafter fired to approximately 2600°F. at a controlled cycle for, for example, fifteen (15) to twenty-six (26) hours to produce a ceramic bond. The refractory so used can be utilized in a conventional manner as a refractory in a glass furnace.

As will be apparent to one skilled in the art, various modifications can be made within the scope of the 55 aforesaid description. Such modifications being within the ability of one skilled in the art form a part of the present invention and are embraced by the appended claims.

#### CLAIMS

- 60 1. The method of making a refractory which is resistant to alkali vapors comprising: forming a mixture comprising as essential components silica 10-16%, alumina 67-75%, and zirconia 14-20%, said silica being essentially tied up in zircon; forming said mixture into a moldable mass; and molding said mass into a shaped refractory. 60

2. The method of claim 1 wherein said moldable mass includes an electrolyte and water.
3. The method of claim 2 wherein at least one of the essential components is in the form of inorganic bubbles.
4. The method of either of claims 2 or 3 wherein said alumina is at least partially in the form of bubbles.
- 5 5. The method of any one of claims 1 to 4 wherein said refractory is shaped to form at least a part of the superstructure of a glass furnace forehearth. 5
6. A method of making a refractory substantially as hereinbefore described and illustrated by the foregoing example.
7. A refractory composition consisting essentially of silica ( $\text{SiO}_2$ ) 10-16%, alumina ( $\text{Al}_2\text{O}_3$ ) 67-75%,  
10 zirconia ( $\text{ZrO}_2$ ) 14-20%, and other oxides 0-2%. 10
8. The refractory of claim 7 wherein said silica is present at 15.9%, said alumina is present at 68.3%, and said zirconia is present at 15.7%.
9. The refractory composition of either of claims 7 or 8, with said composition being partially in the form of inorganic bubbles.
- 15 10. A refractory composition substantially as hereinbefore described and illustrated by the foregoing Example. 15
11. A refractory composition when produced by a method in accordance with any one of claim 1 to 6.
12. An article formed from a refractory composition according to any one of claims 7 to 11.

Printed in the UK for HMSO, D8816935, 3/85, 7102.

Published by The Patent Office, 28 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.